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Photochemical Reactions of Poly(1-pyrazolyl)boratotricarbonylmanganese(I) with Phosphorus Donor Ligands

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Received March 30, 1971

The photochemical syntheses of $PzB(Pz)_3Mn(CO)_{3-n}L_n$ (Pz = 1-pyrazolyl; L = $P(OCH_3)_3$ and $P(OC_6H_5)_3$, n = 1, 2; $P(CH_3)_3$, $P(C_6H_5)_3$, $P(i\text{-}C_3H_7)_3$, $P(n\text{-}C_4H_9)_3$, and $P(C_6H_{11})_3$, n = 1) and $HB(CH_3PzCH_3)_3Mn(CO)_2L$ (CH_3PzCH_3 = 3,5-dimethyl-1-pyrazolyl; L = $P(OCH_3)_3$, $P(OC_6H_5)_3$, and $P(CH_3)_3$) have been accomplished. A comparison of the products obtained from the CH_3-substituted pyrazolylborate tricarbonyl compounds with those obtained from unsubstituted pyrazolylborate tricarbonyl compounds indicates that the steric effects of the ligands control the degree of substitution in reactions of this type. Chemical, physical, and electronic properties of these compounds are compared with those of the analogous π-cyclopentadienyltricarbonylmanganese(I) derivatives.

Introduction

The use of poly(1-pyrazolyl)borate anions[1-3] as ligands in transition metal complexes has been reported.[4-7] Two of these complexes,[6] tetrakis(1-pyrazolyl)boratotricarbonylmanganese(I) [$PzB(Pz)_3Mn(CO)_3$] and hydrotris(3,5-dimethyl-1-pyrazolyl)boratotricarbonylmanganese(I) [$HB(CH_3PzCH_3)_3Mn(CO)_3$], are air-stable, crystalline solids in which the pyrazolylborate anion serves as a uninegative, tridentate ligand (Figure 1). These compounds are structurally related to the half-sandwich compounds π-$C_5H_5Mn(CO)_3$,[8] π-$C_4H_4NMn(CO)_3$,[9-11] and $(1,7\text{-}B_9H_9CHPCH_3)Mn(CO)_3$.[12]

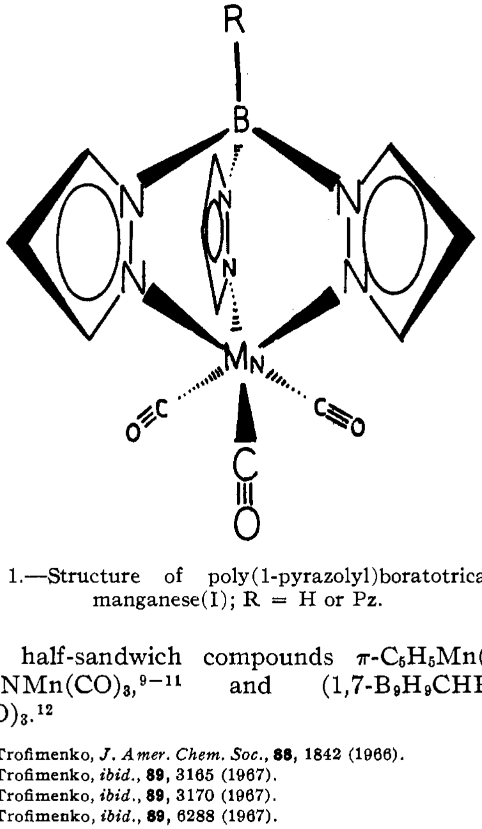

Figure 1.—Structure of poly(1-pyrazolyl)boratotricarbonylmanganese(I); R = H or Pz.

The ability of π-$C_5H_5Mn(CO)_3$ to undergo photochemical substitution of one or two carbonyl groups by nitrogen, oxygen, sulfur, phosphorus, or olefin containing ligands is well known.[13-16] Similar photochemical

$$\pi\text{-}C_5H_5Mn(CO)_3 + nL \xrightarrow{h\nu} \pi\text{-}C_5H_5Mn(CO)_{3-n}L_n + nCO$$

reactions have been reported[11] for π-$C_4H_4NMn(CO)_3$ with triphenylphosphine, -arsine, or -stibine. As part of our comparison of the properties of the cyclopentadienide and poly(1-pyrazolyl)borate anions as ligands, photochemical reactions of $PzB(Pz)_3Mn(CO)_3$ and $HB(CH_3PzCH_3)_3Mn(CO)_3$ with several phosphines and phosphites have been investigated.

Experimental Section

All syntheses were carried out under a nitrogen atmosphere. In addition, procedures which involved handling the air-sensitive ligands $P(CH_3)_3$, $P(i\text{-}C_3H_7)_3$, and $P(C_6H_{11})_3$ were carried out in an inert-atmosphere box.

Infrared solution spectra were measured on a Perkin-Elmer Model 180 spectrophotometer using Fisher spectroscopic grade cyclohexane in 1.0-mm cells equipped with NaCl windows. Carbonyl frequencies are estimated to be accurate to ±1 cm^{-1}. Microanalyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, Bonn, Germany, and by Chemalytics Inc., Tempe, Ariz.

Materials.—π-$C_5H_5Mn(CO)_3$ and $Mn_2(CO)_{10}$ were obtained as gifts from Ethyl Corporation. Potassium tetrakis(1-pyrazolyl)borate [$KB(Pz)_4$] and potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate [$KHB(CH_3PzCH_3)_3$] were prepared by the method of Trofimenko.[3-4] The compounds $Mn(CO)_5Br$,[17] $PzB(Pz)_3Mn(CO)_3$,[6] and $HB(CH_3PzCH_3)_3Mn(CO)_3$[6] were all prepared by literature methods.

Ligands.—Trimethyl phosphite (Eastman), tributyl phosphite (Eastman), triphenyl phosphite (Eastman), trimethylphosphine (Strem), triisopropylphosphine (Pfaltz and Bauer), and phosphorus trichloride (J. T. Baker) were all used without further purification. Triphenylphosphine (Strem) was recrystallized from methanol. Phosphorus trifluoride (ROC/RIC) was passed through a trap at −78° before use. Tricyclohexylphosphine was obtained as a gift from Dr. G. Eberhardt of Sun Oil Company and purified by recrystallization from ligroin under a nitrogen atmosphere. Tris(pentafluorophenyl)phosphine was prepared by the method previously described.[18]

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[1] S. Trofimenko, *J. Amer. Chem. Soc.*, **88**, 1842 (1966).

[2] S. Trofimenko, *ibid.*, **89**, 3165 (1967).

[3] S. Trofimenko, *ibid.*, **89**, 3170 (1967).

[4] S. Trofimenko, *ibid.*, **89**, 6288 (1967).

[5] J. P. Jesson, S. Trofimenko, and D. R. Eaton, *ibid.*, **89**, 3148 (1967).

[6] S. Trofimenko, *ibid.*, **91**, 588 (1969).

[7] S. Trofimenko, *Inorg. Chem.*, **8**, 2675 (1969).

[8] E. O. Fischer and R. Jira, *Z. Naturforsch. B*, **9**, 618 (1954).

[9] K. K. Joshi and P. L. Pauson, *Proc. Chem. Soc., London*, 326 (1962).

[10] K. K. Joshi, P. L. Pauson, A. R. Qazi, and W. H. Stubbs, *J. Organometal. Chem.*, **1**, 471 (1964).

[11] R. B. King and A. Efratz, *ibid.*, **20**, 264 (1969).

[12] J. L. Little, P. S. Welcker, N. J. Log, and L. J. Todd, *Inorg. Chem.*, **9**, 63 (1970).

[13] W. Strohmeier, *Angew. Chem.*, **76**, 873 (1964); *Angew. Chem., Int. Ed. Engl.*, **3**, 730 (1964).

[14] W. Strohmeier and F. J. Müller, *Chem. Ber.*, **100**, 2812 (1967).

[15] E. Koerner von Gustorf and F. W. Grevels, *Fortschr. Chem. Forsch.*, **13**, 366 (1969).

[16] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970, Chapter 17.

[17] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

[18] R. D. W. Kemmitt, D. I. Nichols, and R. D. Peacock, *ibid.*, *A*, 2149 (1968).

TABLE I

PREPARATION, PROPERTIES, AND ANALYTICAL DATA

					Anal					
					% C		% H		% N	
Compound	Method (solvent)	Time, hr	Uncorrected mp, °C	% yield	Calcd	Found	Calcd	Found	Calcd	Found
$PzB(Pz)_3Mn(CO)_2P(C_6H_5)_3$	A (benzene)	3	190–192	45	58.9	58.7	4.4	4.2	17.0	17.2
$PzB(Pz)_3Mn(CO)_2P(OC_6H_5)_3$	B (THF)	4	149	26	54.9	55.0	3.9	3.9	16.0	15.8
$PzB(Pz)_3Mn(CO)[P(OC_6H_5)_3]_2$	A (benzene)	6	150 dec	38	59.6	59.3	4.3	4.4	11.4	11.6
$PzB(Pz)_3Mn(CO)_2P(OCH_3)_3$	B (THF)	4	175	37	39.7	39.7	4.1	4.1	21.8	21.7
$PzB(Pz)_3Mn(CO)[P(OCH_3)_3]_2$	A (benzene)	5.5	134 dec	33	37.4	37.2	5.0	5.1	18.4	18.5
$PzB(Pz)_3Mn(CO)_2P(n\text{-}C_4H_9)_3$	A (THF)	2.5	136	54	52.7	52.7	6.6	6.6	19.0	19.1
$PzB(Pz)_3Mn(CO)_2P(i\text{-}C_3H_7)_3$	A (THF)	3	149–150	53	50.2	50.8	6.0	6.0	20.4	20.6
$PzB(Pz)_3Mn(CO)_2P(CH_3)_3$	A (THF)	3	220–221	36	43.8	44.1	4.6	4.7	24.0	23.7
$PzB(Pz)_3Mn(CO)_2P(C_6H_{11})_3$	A (THF)	3.5	152–154	46	57.3	57.4	6.8	6.6	16.7	16.8
$HB(CH_3PzCH_3)_3Mn(CO)_2P(CH_3)_3$	A (THF)	3.5	135 dec	32	50.0	50.1	6.5	6.5	17.4	17.6
$HB(CH_3PzCH_3)_3Mn(CO)_2P(OCH_3)_3$	A (THF)	4.5	175 dec	25	45.1	45.0	5.9	5.9	15.9	16.0
$HB(CH_3PzCH_3)_3Mn(CO)_2P(OC_6H_5)_3$	A (THF)	5	165 dec	17	58.5	58.4	5.2	5.2	11.7	11.8

Syntheses. 1. Monosubstituted Derivatives of Tetrakis(1-pyrazolyl)boratotricarbonylmanganese(I) and Hydrotris(3,5-dimethyl-1-pyrazolyl)boratotricarbonylmanganese(I).—Monosubstituted compounds were prepared by one of the following methods. Reaction times, method used, and analytical data are given in Table I. No derivatives of the type $HB(CH_3PzCH_3)_3Mn(CO)_2L$ were obtained with $P(i\text{-}C_3H_7)_3$, $P(C_6H_5)_3$, $P(C_6H_{11})_3$, or PCl_3.

Direct Method A.—A benzene or THF solution containing 1 mmol of the tricarbonyl compound and 1.1 mmol of the phosphine or phosphite was irradiated in a Pyrex flask using a 100 W, General Electric, long-wavelength (3660 Å), spot-type mercury light. Upon reduction of the volume of solvent *in vacuo* to 5 ml, addition of 25 ml of ethanol, and cooling, a crystalline solid was precipitated. Purification was accomplished by chromatography on a 2 × 25 cm acid-washed alumina column using dichloromethane–hexane mixtures as the eluent.

Indirect Method B.[19]—A solution of the tricarbonyl compound (1 mmol) in THF (35 ml) was irradiated in a Pyrex flask at 0–10° for 4 hr. The solution gradually turned deep red as CO was evolved. Irradiation was discontinued, 1.1 mmol of the phosphine or phosphite added, and the solution warmed for 5 min. The solution changed from red to light yellow. Removal of solvent and chromatographic purification gave the crystalline product.

2. Disubstituted Derivatives of Tetrakis(1-pyrazolyl)boratotricarbonylmanganese(I).—The compounds $PzB(Pz)_3Mn(CO)L_2$ [$L = P(OCH_3)_3$ and $P(OC_6H_5)_3$] were prepared by the above method A using an excess of ligand. No disubstituted product was obtained with $P(CH_3)_3$, $P(i\text{-}C_3H_7)_3$, $P(n\text{-}C_4H_9)_3$, $P(C_6H_{11})_3$, or $P(C_6H_5)_3$. PF_3 gave products which had ir spectra characteristic of $PzB(Pz)_3MnCO(PF_3)_2$ and $HB(CH_3PzCH_3)_3Mn(CO)(PF_3)_2$, but they were not obtained in a pure state.

3.—The compounds $\pi\text{-}C_5H_5Mn(CO)_2L$ [$L = PF_3$, PCl_3, $P(OCH_3)_3$, $P(OC_6H_5)_3$, $P(CH_3)_3$, $P(C_6H_{11})_3$, $P(i\text{-}C_3H_7)_3$, $P(n\text{-}C_4H_9)_3$, and $P(C_6H_5)_3$] were prepared by methods previously reported.[14]

Results and Discussion

Phosphine and phosphite derivatives of tetrakis(1-pyrazolyl)boratotricarbonylmanganese(I) and hydrotris(3,5-dimethyl-1-pyrazolyl)boratotricarbonylmanganese(I) are air-stable, crystalline solids whose colors range from pale yellow to deep orange-yellow. The compounds are insoluble in water, slightly soluble in ethanol and saturated hydrocarbon solvents, and quite soluble in aromatic solvents, dichloromethane, carbon disulfide, and acetone. Disubstituted derivatives are less soluble than the corresponding monosubstituted compounds. Solutions of these compounds are more air sensitive than the pure solids, but extensive decomposition is not observed in deoxygenated solvents even after several days.

Two general synthetic methods were used. Method A, which involves direct photochemical reaction of the tricarbonyl compound with the ligand, was used to prepare monosubstituted derivatives whenever no disubstitution was observed. This method was also employed for the synthesis of disubstituted products.

In those cases in which disubstitution occurs in the direct reaction of the tricarbonyl compound with the ligand, monosubstituted derivatives were prepared by the photochemical reaction of the tricarbonyl compound with THF, followed by *in situ* reaction of the red THF derivative[20] with the desired phosphine or phosphite.

Infrared Spectra—The frequencies of the carbonyl stretching vibrations in the infrared spectra of the poly(1-pyrazolyl)borate complexes are given in Table II.

TABLE II

IR FREQUENCIES IN CYCLOHEXANE (CM^{-1})

	$\pi\text{-}C_5H_5Mn(CO)_2L$		$PzB(Pz)_3Mn(CO)_2L$		$HB(CH_3PzCH_3)_3Mn(CO)_2L$	
L	A′	A″	A′	A″	A′	A″
CO	2028	1946	2042	1941	2032	1927
PF_3	1998	1942	2000	1940	1988	1925
PCl_3	1995	1944	1998	1937	. . .	. . .
$P(OC_6H_5)_3$	1970	1909	1974	1901	1961	1883
$P(OCH_3)_3$	1954	1891	1961	1887	1949	1869
$P(C_6H_5)_3$	1945	1884	1945	1870	. . .	. . .
$P(CH_3)_3$	1939	1876	1941	1865	1927	1840
$P(n\text{-}C_4H_9)_3$	1935	1872	1937	1861	1903	1820[a]
$P(i\text{-}C_3H_7)_3$	1937	1872	1937	1861	. . .	. . .
$P(C_6H_{11})_3$	1931	1869	1935	1859	. . .	. . .

Disubstituted Compounds

$PzB(Pz)_3Mn(CO)(PF_3)_2$	1958	$PzB(Pz)_3Mn(CO)[P(OCH_3)_3]_2$	1871
$PzB(Pz)_3Mn(CO)[P(OC_6H_5)_3]_2$	1895[b]	$HB(CH_3PzCH_3)_3Mn(CO)(PF_3)_2$	1948

[a] In THF. [b] In CS_2.

Frequencies decrease in the order $L = PF_3 > PCl_3 > P(OC_6H_5)_3 > P(OCH_3)_3 > P(C_6H_5)_3 > PR_3$. This is the same order found in the compounds $C_5H_5Mn(CO)_2L$.[14,21] CO stretching frequencies are generally assumed to be primarily a reflection of the amount of $d\pi\text{-}p\pi$ back-bonding to π^* orbitals of carbon monoxide; therefore, a lowering of ν_{CO} in a series of similar compounds indicates an increase of electron density on the metal as a result of the noncarbonyl ligands. Since either an increase in donor strength or a decrease in acceptor ability of a ligand increases the electron density on the metal, the observed trend in carbonyl stretching

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[19] This method was described previously for $C_5H_5Mn(CO)_3$; see W. Strohmeier, C. Barbeau, and D. von Hobe, *Chem. Ber.*, **96**, 3254 (1963).

[20] Although the THF derivative was never isolated, the infrared spectrum of the irradiated red mixture contained bands at 1825 and 1948 cm^{-1} in THF. These were attributed to the presence of $PzB(Pz)_3Mn(CO)_2THF$.

[21] W. Strohmeier and F. J. Muller, *Z. Naturforsch. B*, **22**, 451 (1967).

frequencies is consistent with accepted trends in basicity and acceptor ability for phosphorus ligands.[22-24]

Although the antisymmetric carbonyl stretching vibrations for $PzB(Pz)_3Mn(CO)_2L$ consistently occur at somewhat lower frequencies than those for π-$C_5H_5Mn(CO)_2L$, the symmetric stretching vibrations occur at slightly higher frequencies for the pyrazolylborate derivatives.[25-27] It appears, therefore, that the net electronic effect of the pyrazolylborate group is similar to that of the cyclopentadienyl group, although the partitioning of the electronic character in terms of donor and acceptor strengths may be significantly different in the two cases.

Steric Effects—Tolman[28] has reported results of phosphine and phosphite ligand exchange studies in zerovalent nickel complexes. Using molecular models to approximate cone angles[29] for the ligands, he concluded that steric effects are dominant in determining the stability of the complexes. Values of the cone angles along with the degree of substitution obtained with various ligands in our studies are listed in Table III.[30] The results strongly suggest that the degree of substitution is dependent upon the size of the ligand L. Irradiation of $PzB(Pz)_3Mn(CO)_3$ produces both mono- and disubstitution with PF_3,[31] $P(OCH_3)_3$, and $P(OC_6H_5)_3$, while only the monosubstituted product is obtained with the bulkier ligands PCl_3, $P(C_4H_9)_3$, $P(C_6H_5)_3$, $P(i\text{-}C_3H_7)_3$, $P(CH_3)_3$, and $P(C_6H_{11})_3$. No reaction is observed with the very bulky $P(C_6F_5)_3$. Irradiation of $HB(CH_3PzCH_3)_3Mn(CO)_3$, in which the steric requirements of the pyrazolylborate group have been increased by the presence of methyl substituents, leads to mono- and disubstitution with PF_3 and monosubstitution with $P(OCH_3)_3$, $P(OC_6H_5)_3$, and $P(CH_3)_3$. No substituted product was obtained with the other phosphines.[32]

TABLE III

COMPARISON OF CONE ANGLES WITH DEGREE OF SUBSTITUTION

Ligand	Cone angle,[a] deg	$PzB(Pz)_3Mn(CO)_{3-n}L_n$	$HB(CH_3PzCH_3)_3Mn(CO)_{3-n}L_n$
PF_3	104 ± 2	1, 2	1, 2
$P(OCH_3)_3$	107 ± 2	1, 2	1
$P(OC_6H_5)_3$	121 ± 10	1, 2	1
$P(CH_3)_3$	118 ± 4	1	1
PCl_3	125 ± 2	1	0
$P(C_4H_9)_3$	130 ± 4	1	1[b]
$P(C_6H_5)_3$	145 ± 2	1	0
$P(i\text{-}C_3H_7)_3$	160 ± 10	1	0
$P(C_6H_{11})_3$	179 ± 10	1	0
$P(C_6F_5)_3$	184 ± 2	0	0

[a] Taken from ref 28. [b] Seen only in solution.

A comparison of the carbonyl stretching frequencies for monosubstituted derivatives with the degree of substitution obtained with a given ligand indicates that in general a higher degree of substitution is obtained with ligands which give compounds having higher CO stretching frequencies than with those which produce compounds having lower CO stretching frequencies. Therefore, one might argue that the electronic properties of the ligand play an important role in determining the degree of substitution.[33-35] If this were the case, one would expect $P(CH_3)_3$ and $P(C_6H_5)_3$ to give analogous compounds, based on the similarity in frequencies. However, $HB(CH_3PzCH_3)_3Mn(CO)_3$ forms no product when irradiated in the presence of $P(C_6H_5)_3$, while $P(CH_3)_3$ produces $HB(CH_3PzCH_3)_3Mn(CO)_2P(CH_3)_3$. Also, the observation that no derivative is formed with $P(C_6F_5)_3$, in spite of the fact that electronically it is similar to PCl_3 and $P(OC_6H_5)_3$,[36] suggests that steric factors predominate.

Acknowledgments—Financial assistance by the University of Delaware Research Foundation is gratefully acknowledged. We also wish to thank Ethyl Corporation for gifts of π-$C_5H_5Mn(CO)_3$ and $Mn_2(CO)_{10}$ and Dr. G. Eberhardt and Mr. J. Melpolder for samples of phosphines. We are indebted to Dr. S. Trofimenko for providing initial samples of the carbonyl compounds and for helpful discussions.

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(22) C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

(23) E. M. Thorsteinson and F. Basolo, *J. Amer. Chem. Soc.*, **88**, 3929 (1966).

(24) W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).

(25) Similar results have been observed previously for $PzB(Pz)_3Mo(CO)_2NO$ (ν_{CO} 2024, 1937 cm^{-1})[7] and π-$C_5H_5Mo(CO)_2NO$ (ν_{CO} 2021, 1948 cm^{-1}).[26] However, both frequencies are lower for $PzB(Pz)_3Mo(CO)_2N_2C_6H_5$ (ν_{CO} 1996, 1913 cm^{-1})[7] than for π-$C_5H_5Mo(CO)_2N_2C_6H_5$ (ν_{CO} 2000, 1928 cm^{-1}).[27] Thus, one must exercise caution in using carbonyl stretching frequencies as a basis of a discussion of electronic effects.

(26) R. B. King, *Inorg. Chem.*, **5**, 2242 (1966).

(27) R. B. King and M. B. Bisnette, *ibid.*, **5**, 300 (1966).

(28) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

(29) The cone angle is the angle, having an apex at the metal, required to contain the outermost atoms of a ligand. It is, therefore, a measure of the size of the ligand.

(30) Although the absolute values of the cone angles will be different in Mn(I) compounds than in those with Ni(0), the relative magnitudes for various ligands should be accurately reflected by the Ni(0) data.

(31) Although good analyses were not obtained for the PF_3 and PCl_3 derivatives, their existence is indicated by the infrared spectra of the solid products obtained from photochemical reactions.

(32) $HB(CH_3PzCH_3)_3Mn(CO)_2P(n\text{-}C_4H_9)_3$ was observed in solution but not isolated.

(33) W. Strohmeier and J. F. Guttenberger, *Chem. Ber.*, **97**, 1256 (1964).

(34) W. Strohmeier and H. Hellmann, *ibid.*, **97**, 1877 (1964).

(35) W. Strohmeier, G. Popp, and J. F. Guttenberger, *ibid.*, **99**, 165 (1966).

(36) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2953 (1970).